AD-A126 480 STRUCTURAL AND VIBRATIONAL EXCITATIONS OF INTERCALATED GRAPHITE(U) MICHIGAN STATE UNIV EAST LANSING DEPT OF PHYSICS AND ASTRONOMY S A SOLIN 22 MAR 83 25 1/1

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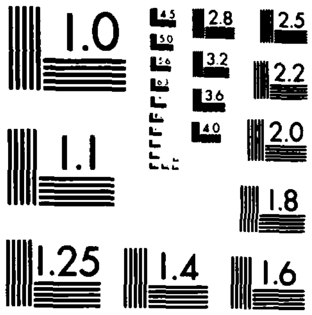

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Raman and IR Studies of GIC's
Phase Transitions in GIC's
Staging Effects

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have used diffuse and discrete temperature-dependent and pressure-dependent x-ray diffraction studies and Raman scattering to study the structure and vibrational excitations of graphite intercalation compounds (GIC's).

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Final Report for U.S. Army Contract DAAG 29-80-K-0003

The contract cited above was awarded while the principal investigator (PI) was on the faculty of the University of Chicago and was transferred to Michigan State University in 1980, after the PI joined the faculty there.

The focus of the supported research was the study of the structure and vibrational excitations of graphite intercalation compounds (GIC's) using primarily diffuse and discrete temperature-dependent and pressure-dependent x-ray diffraction studies and Raman scattering.

Much of the important structure results of this work are summarized in an extensive review article entitled, "The Nature and Structural Properties of Graphite Intercalation Compounds," (#4 on the list of publications). Similarly, the early results on vibrational studies are summarized in another review article entitled, "Raman and IR Studies of Graphite Intercalates," (#12 on the list of publications).

Our major contributions in the supported research were:

1. The discovery and analysis of new structural phases and novel phase transitions in GIC's.
2. The discovery of pressure-dependent staging effects which significantly alter both light scattering and x-ray results;
3. The discovery and quantitative characterization of carbon layer distortions in GIC's.

During the MSU period of the above-referenced grant, a subcontract was issued to Professor S.C. Moss of the University of Houston. Professor Moss and his colleagues have made significant contributions to the research program. In particular, they have effectively explored computer models of the disordered structures of alkali GIC's.

The enclosed preprint contains detailed descriptions of our most recent work.

List of Publications

U.S. Army Research Office Contract DAAG 29-80-K-0003

1. "In-Plane Ordering in Stage-2 Graphite Intercalation Compounds," C. Horie, S.A. Solin, H. Miyazaki, S. Igarashi, and S. Hatakeyama, Phys. Rev. B 27, 3796 (1983).

2. "Intercalate Lattice Dynamics in Stage-1 Rubidium Graphite," W. Kamitakahara, N. Wada, and S.A. Solin, Solid State Comm. 44, 297 (1982).

3. "Neutron Spectroscopy of Phonons in Stage-1 Rubidium Graphite," W.A. Kamitakahara, N. Wada, S.A. Solin, and L.M. Seaverson, Phys. Rev. B (submitted).

4. "The Nature and Structural Properties of Graphite Intercalation Compounds," S.A. Solin, Adv. in Chem. Phys. 49, 455 (1982).

5. "Novel Structural Properties of Graphite Intercalation Compounds," S.A. Solin, Novel Materials and Techniques in Condensed Matter, ed. by G.W. Crabtree and P. Vashishta (North-Holland, New York, 1982), p. 253.

6. "Structural Study of Stage-1 Cesium Graphite at High Temperature," N. Caswell, Phys. Rev. (in press).

7. "High Pressure X-Ray and Raman Studies of Rb and Cs Graphite Intercalation Compounds," N. Wada, Phys. Rev. B 24, 2 (1981).

8. "Pressure Dependent X-Ray Studies of Alkali Graphite Intercalation Compounds," N. Wada and S.A. Solin, Physica 105B, 268 (1981).

9. "X-Ray Compressibility Measurements of the Graphite Intercalates KC_8 and KC_{24}," N. Wada, Roy Clarke, and S.A. Solin, Solid State Comm. 35, 675 (1980).

10. "X-Ray Diffraction Measurements of the Quantitative and Qualitative Effects of Pressure on Pristine Graphite," N. Wada, R. Clarke, and S.A. Solin, Synthetic Metals 2, 27 (1980).

11. "Pressure-Induced Staging Transition in KC_{24}," Roy Clarke, N. Wada, and S.A. Solin, Phys. Rev. Lett. 44, 1616 (1980).

12. "Raman and IR Studies of Graphite Intercalates," S.A. Solin, Physica 99B, 443 (1980).

13. "Variations in the Classical Model of Staging in Graphite Intercalates: EXAFS Results," N. Caswell, S.A. Solin, T.M. Hayes, and S.J. Hunter, Physica 99B, 463 (1980).

14. "X-Ray Study of Intercalate Order-Disorder Transition in $C_{24}K$," H. Zabel, S.C. Moss, N. Caswell, and S.A. Solin, Phys. Rev. Lett. 43, 2022 (1979).

15. "Mass- and Charge-Density Modulation of Graphite in Potassium-Graphite Intercalates," M. Mori, S.C. Moss, Y.M. Jan, and H. Zabel, Phys. Rev. B 25, 1287 (1982).

16. "Lattice Gas Disorder in Alkali-Graphite Intercalates and Other 2D Systems," S.C. Moss and H. Zabel, Surface Science 97, L357 (1980).

17. "2-D Potassium Structures in the Disordered Phases of $C_{12n}K$ (n=2,3,4)," H. Zabel, Y.M. Jan, and S.C. Moss, Physica 99B, 453 (1980).

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NEUTRON SPECTROSCOPY OF PHONONS IN RbC_8

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Abstract.- Neutron scattering methods have been used to investigate the lattice dynamics of stage-one Rb graphite. Intercalate (Rb) modes with polarizations and wave vectors parallel to the basal plane have been observed for the first time. The experimentally-derived partial phonon density of states for intercalate modes is compared with model calculations. Phonon dispersion curves have been measured for longitudinal c-axis modes and for some transverse modes propagating in the basal plane.

1. Experiment.- A large (6 cm^3) sample was prepared by the usual two-bulb method[1] from Union Carbide ZYH pyrolitic graphite. The crystallites in such a sample are aligned with a common c-axis but are randomly oriented in the ab plane. A triple-axis spectrometer at the Oak Ridge Research Reactor was used to carry out the neutron scattering measurements.

2. Intercalate Modes.- By these we mean phonons for which the motions involved are almost completely those of the intercalate (Rb) atoms, with wave vectors and displacements parallel to the basal plane. By averaging spectra for a number of wave vector transfers Q in the basal plane, we have been able to obtain a partial phonon density of states for the intercalate modes, as shown in Fig. 1. In the low-energy region shown, for such scans with $\vec{Q}$ parallel to the basal plane, the graphite host responds only very weakly because of the very strong forces opposing intralayer in-plane displacements of C atoms. The general room background and inelastic scattering from the graphite planes (determined by a scan on pure pyrolitic graphite) gave a smooth, gently sloping contribution to the observed spectra which was subtracted off in order to obtain the intercalate mode spectrum. The latter was then converted to a phonon density of states by dividing by well-known factors in the one-phonon neutron cross section.

The data shown in Fig. 1 were compared with several model calculations. In no case were we able to obtain good agreement with models considering only

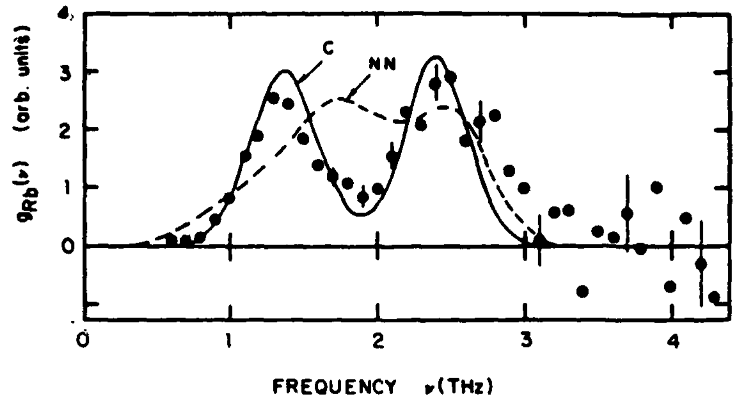

Fig. 1 : Points are the experimentally-derived partial phonon density of states for intercalate modes. Calculation NN results from a two-dimensional (2D) nearest-neighbor force model, while C represents a 3D unscreened Coulomb force model.

short-range (i.e., nearest-neighbor) forces between Rb atoms. On the other hand, it was found that a model in which the Rb-Rb forces were simply the unscreened Coulomb interactions between +1 ions gave a good description of the intercalate mode phonon density of states (see curve C in Fig. 1). This model has only one adjustable parameter, representing the short-range C-Rb forces, which creates a low-frequency cutoff to the spectrum, and shifts all modes to somewhat higher frequencies. The overall shape of the spectrum and the general magnitude of the frequencies arise from the crystal structure and the Coulomb interaction, for which we need to introduce no additional parameters. The good agreement with experiment shows that conduction electron screening of the Rb motions, although it must be present, has a much less important effect on the intercalate phonon spectrum in RbC_8 than on the lattice dynamics of pure Rb metal.[2,3] The unusual order-disorder phase transformations which occur[4,5] in RbC_8 and similar[5] compounds must closely involve the intercalate-intercalate and intercalate-graphite interactions about which we have obtained detailed information through our experiment and its analysis.

3. Phonon Dispersion Curves.- In addition to our observations of intercalate modes, we have also made measurements on phonon dispersion in RbC_8. The longitudinal interlayer frequencies for modes propagating along the c-axis are in generally good agreement with the previous measurements of Ellenson et al.[4] Dispersion curves for transverse modes with polarization perpendicular to the basal plane, but with wave vector in the basal plane, were also measured, and are shown in the right hand side of Fig. 2. Because our sample is c-oriented and not a single crystal, these dispersion relations are averages over all directions in the basal plane. However, as in pure graphite,[6] $\omega(\vec{q})$ is bound to be rather isotropic for $\vec{q}$ in the basal plane. The lowest of these transverse branches lies substantially lower than in pure graphite,[6] despite the fact that the strong intralayer C-C forces which largely determine these modes in pure graphite are unlikely to be much different in RbC_8. Qualitatively, this points to a disproportionate participation of Rb motions (i.e., large Rb phonon

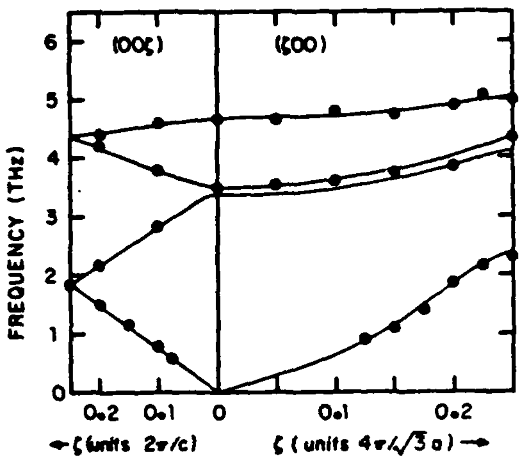

Fig. 2 : Phonon dispersion curves for RbC_8.

eigenvectors) for these modes in the intercalation compound. Recently proposed lattice dynamical models[7,8] should be useful in analysing our results.

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